Rapid Synthesis and Characterization of an Oxygen-Deficient Defect Perovskite La₄BaCu₅O₁₃₊δ Phase

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Oxygen-deficient defect perovskite La₄BaCu₅O₁₃₊δ phase has been synthesized by the nitrate-citrate gel combustion method at 950°C for 2 h. Structural parameters were refined by the Rietveld refinement method using room-temperature powder XRD data. The La₄BaCu₅O₁₃₊δ crystallizes in the tetragonal structure with space group P4/m (no. 83) and having the lattice parameters \( a = 8.6508(1) \) Å and \( c = 3.8606(2) \) Å, respectively. Oxygen content was determined by the iodometric titration. Low-temperature resistivity result reveals that La₄BaCu₅O₁₃₊δ compound exhibit metallic behavior up to 15 K.

1. Introduction

The oxygen-deficient defect perovskite of the formula La₄BaCu₅O₁₃₊δ, first reported by Michel et al. [1] is tetragonal, space group P4/m, \( a \approx \sqrt{5}a_p = 8.644 \) Å, \( c \approx 3.867 \) Å, where \( a_p \) refers to a perovskite sub cell. The model structure [2] consists of groups of four corner-sharing CuO₅ pyramids linked through CuO₆ octahedra in such a way that each octahedron shares four corners with four pyramids and two corners with two other octahedra; each pyramid are connected to four other pyramids and one octahedron. The framework exhibits one perovskite-like tunnel and two hexagonal tunnels per cell. Ba²⁺ and La³⁺ are ordered, with 12-coordinate Ba²⁺ in perovskite tunnels and 10-coordinate La³⁺ in hexagonal tunnels [2, 3]. La₄BaCu₅O₁₃₊δ is unique, because it shows metallic behavior down to lowest possible temperature without undergoing superconducting transition. Mamiya et al. [4] measured the electrical resistivity of La₄BaCu₅O₁₃ compound down to 39 mK without observing superconductivity, because of a three-dimensional network of CuO₅ units. Substitution for the La-site by other rare earth ions in La₄BaCu₅O₁₃₊δ system has been performed by Vijayaraghavan et al. [5]. Oxygen stoichiometry in La₄BaCu₅O₁₃₊δ can be varied to induce a metal-insulator transition [6]. Defect perovskite phases with \( \delta = -0.5 \) and \(-1.0 \) have been identified by Davies and Katzan [3] and also by Kato et al. [7]. We have synthesized La₄BaCu₅₋ₓMₓO₁₃₊δ (M = Ni, Co, 0.0 ≤ X ≤ 1.0; Fe, X ≤ 0.5) by low-temperature NaOH–KOH flux methods [8, 9]. Further, we have shown [10] an anisotropic electrical transport property in La₄BaCu₅₋ₓMₓO₁₃₊δ (M = Ni, Co, Fe, Zn) by conventional solid state method at 1000°C for 48 h.

However, a wet chemical route such as nitrate-citrate gel combustion route can be excellent method for the synthesis of pure multicomponent oxides. Potential advantages of wet chemical route over the conventional solid state reaction method include better homogeneity, better compositional control, and lower processing temperatures [12]. In the present study, nitrate-citrate gel combustion method was employed to prepare oxygen deficient defect perovskite La₄BaCu₅O₁₃₊δ phase and report the structure and electrical properties.

2. Experimental

Stoichiometric amounts of high-purity precalcined La₂O₃ (at 800°C), Ba(NO₃)₂, and CuO were dissolved in 10 mL
Figure 1: Powder X-ray diffraction patterns of La$_4$BaCu$_5$O$_{13.20}$ compound (a) as prepared (before calcination) and (b) calcined at 950°C for 2 h.

Figure 2: Observed, calculated and the difference Rietveld refined X-ray diffraction patterns of La$_4$BaCu$_5$O$_{13.20}$ compound sintered at 850°C for 12 h.

Figure 3: Crystal structure of La$_4$BaCu$_5$O$_{13.20}$ compound.

of HNO$_3$ (8 N) and the required amount of citric acid solution was added. The resulting clear solution was slowly evaporated on a hot plate to dryness followed by calcined at elevated temperature to yield final product. A typical run included the following steps: La$_2$O$_3$ (1.3033 g), Ba(NO$_3$)$_2$ (0.5227 g), and CuO (0.7955 g) were dissolved in 10 mL of HNO$_3$ (8 N), citric acid (6.1478 g) was dissolved in 100 mL of distilled water and added to the metal ions—containing nitrate solution. The clear green color solution was evaporated on hot plate ∼80°C, to form a thick viscous gel. The resulting gel was heated until it turned into a black porous mass, which on continued heating on hot plate, slowly burned to yield black powder. The resulting powder was X-ray amorphous in nature. To obtain crystallinity, black powder was calcined at 950°C for 2 h. The calcined sample was characterized by powder X-ray diffraction (XRD) using PANalytical X’pert pro diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation equipped with X’cellerator. For Rietveld refinement, data were collected at a scan rate of 1°/min. with a 0.02° step size for 2θ from 10° to 100°. The data were refined using the FullProf Suite-2000 version. Morphology and compositional analysis were carried out in a scanning electron microscope (SEM) fitted with an energy dispersive X-ray analyzer (EDX). Electrical resistivity measurement was carried out on sintered pellets (850°C, 12 h) by a four-probe method in the temperature range from 300 to 15 K.

2.1. Determination of Oxygen Content. Oxygen content was determined by iodometric titration [8]. Typically, about 50 mg of the compound was dissolved in 10 mL of HCl (6 N) containing about 1 g of solid KI. Liberated iodine was titrated
Table 1: Rietveld refined structural parameters for La$_4$BaCu$_5$O$_{13+\delta}$ compound.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Oxidation state</th>
<th>Wyckoff notations</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
</tr>
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<tbody>
<tr>
<td>La1</td>
<td>3</td>
<td>(4k)</td>
<td>0.1280(2)</td>
<td>0.2780(2)</td>
<td>0.5000</td>
<td>1</td>
</tr>
<tr>
<td>Ba1</td>
<td>2</td>
<td>(1d)</td>
<td>0.5000</td>
<td>0.5000</td>
<td>0.5000</td>
<td>1</td>
</tr>
<tr>
<td>Cu1</td>
<td>2.44</td>
<td>(1a)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1</td>
</tr>
<tr>
<td>Cu2</td>
<td>2.44</td>
<td>(4j)</td>
<td>0.4165(5)</td>
<td>0.1719(4)</td>
<td>0.0000</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>$-2$</td>
<td>(1b)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>$-2$</td>
<td>(2e)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.10</td>
</tr>
<tr>
<td>O3</td>
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<td>(4j)</td>
<td>0.2822(2)</td>
<td>0.3936(6)</td>
<td>0.0000</td>
<td>1</td>
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<tr>
<td>O4</td>
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<td>(4j)</td>
<td>0.2244(3)</td>
<td>0.0551(5)</td>
<td>0.0000</td>
<td>1</td>
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<td>O5</td>
<td>$-2$</td>
<td>(4k)</td>
<td>0.4119(8)</td>
<td>0.1501(9)</td>
<td>0.5000</td>
<td>1</td>
</tr>
</tbody>
</table>

Crystal system = tetragonal, lattice parameters, $a = 8.6508(1)$ Å and $c = 3.8606(2)$ Å; space group = $P4/m$ (no. 83); $R$ factors, $R_p = 3.72$, $R_{wp} = 5.27$, $R_{Bragg} = 5.12$, $R_F = 4.97$.

Figure 4: Scanning electron micrographs of La$_4$BaCu$_5$O$_{13+\delta}$ compound (a) calcined powder for 2 h and (b) pellet sintered at 850°C for 12 h.

against standard sodium thiosulphate (0.05 N) solution using starch as an indicator.

3. Results and Discussion

Figure 1, shows the typical powder X-ray diffraction patterns for (a) as formed and (b) calcined at 950°C for 2 h. As can be seen from the Figure 1(a), as formed compound is an amorphous in nature. All metal ions are homogeneous in the mixture and are an amorphous in nature. To obtain crystalline phase calcinations was done at different temperature from 600°C to 1000°C for a period of 2 h. The single crystalline oxygen-deficient defect perovskite, La$_4$BaCu$_5$O$_{13+\delta}$ phase was obtained at 950°C for 2 h. Indexed powder X-ray diffraction pattern for La$_4$BaCu$_5$O$_{13+\delta}$ compound is given in Figure 1(b). Oxygen content was determined by iodometric titration for the calcined sample, the wet chemical analysis results reveal that the average oxidation state of copper was found to be +2.48. The final formula of the compound was La$_4$BaCu$_5$O$_{13+\delta}$. The structure of the La$_4$BaCu$_5$O$_{13+\delta}$ compound was refined by powder X-ray Rietveld analysis. The compound crystallizes in the tetragonal structure with space group $P4/m$ (no. 83) and having the lattice parameters $a = 8.6508(1)$ Å and $c = 3.8606(2)$ Å, respectively. Observed, calculated, and the difference X-ray diffraction patterns for La$_4$BaCu$_5$O$_{13+\delta}$ compound is given in Figure 2, and there is good agreement between observed and calculated pattern. Rietveld refined structural parameters are summarized in Table 1. The refined structural parameters are agreed well with those reported in the literature [2, 8]. Crystal structure of La$_4$BaCu$_5$O$_{13+\delta}$ compound was shown in Figure 3. The structure consists of groups of four corner-sharing CuO$_5$ pyramids linked through CuO$_6$ octahedra. Each octahedron shares four corners with four pyramids and two corners with two other octahedra; each pyramid is connected to four other pyramids and one octahedron. The framework exhibits one perovskite-like tunnel and two hexagonal tunnels per cell. Ba$^{2+}$ and La$^{3+}$ are ordered, with 12-coordinate Ba$^{2+}$ in perovskite tunnels and 10-coordinate La$^{3+}$ in hexagonal tunnels.

The surface morphology and grain sizes of La$_4$BaCu$_5$O$_{13+\delta}$ compound have been investigated by scanning electron microscopy. In Figure 4, shown the micrographs of La$_4$BaCu$_5$O$_{13+\delta}$ phase (a) calcined powder for 2 h and (b) pellet sintered at 850°C for 12 h. From Figure 4(a), the powder sample shows voluminous and porous morphology. The porous nature of combustion derived calcined powder can be attributed to large amount of gases
evolved during combustion reaction. On the other hand sintered pellet at 850°C shows growth in particle sizes and well-defined grain boundary (see Figure 4(b). The agglomerated particles sizes are in the range of 10–20 μm, the micrograph indicate that the sintered pellet shows densification and compactability compared to the calcined powder. Compositional analysis was verified by the energy dispersive X-ray analysis (EDX). The measurements were done on the spot mode and overall area of the sample, and EDX analysis on several spots revealed constancy of compositions.

Four-probe electrical resistivity as a function of temperature measurement was performed on the pellet sintered at 850°C for 12 h. Resistivity as a function of temperature plot of La4BaCu3O13.20 compound is given in Figure 5. The compound shows a positive temperature coefficient of resistivity, typical of a metal down to 15 K, with the resistivity varying from 0.88 mΩcm at 300 K to 0.23 mΩcm at 15 K. The present resistivity value is comparable with those reported in the literature [8].

4. Conclusions

In conclusion, oxygen-deficient defect perovskite La4BaCu3O13.20 phase is successfully synthesized by the rapid nitrate-citrate gel combustion method. Crystal structure was confirmed by the Rietveld refinement method using room-temperature powder XRD data. The compound crystallizes in the tetragonal structure and exhibit metallic property.

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References

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